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PARA-DICHLOROBENZENE AS AN INSECT FUMIGANT.

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INTRODUCTION.

The purpose of the following pages is to determine the insecticidal value of para-dichlorobenzene as a fumigant, as well as to ascertain the injury, if any, to cloth fabrics and the effects of the vapors on plant life as well as upon the germination of seeds.

Para-dichlorobenzene is a definite chemical compound, known for many years, but only recently used as an insecticide. It is a colorless, crystalline substance which volatilizes very readily as a colorless vapor with a peculiar ether-like odor. The vapor is harmless to human beings and domestic animals under ordinary conditions, but in many instances it is a specific poison for insects. It has an additional advantage over the many other fumigants in that the odor does not cling to fabrics, etc., the characteristic ether-like smell rapidly disappearing upon exposure of the fumigated substances to the open air. Probably the greatest advantages that para-dichlorobenzene possesses over other fumigants are its absolute noninflammability and its comparatively low cost of purchase and application in proportion to the result obtained.

EFFECTS OF INHALATION OF THE VAPOR.

As stated, para-dichlorobenzene possesses only a weak ether-like smell, which, owing to the volatile nature of the substance, will pass off in a few hours if exposed to the air. Dr. Curschman, at the Greppin Works in Germany, concludes from a series of experiments that para-dichlorobenzene, when used as an exterminator for moths, etc., is virtually harmless to human beings, perhaps even superior to naphthalene in this respect. He goes further by stating that poisoning by para-dichlorobenzene to human beings through contact with the skin is impossible and that inhalation of the vapors of this product is perfectly harmless. According to him, para-dichloro-

benzene is harmful to human beings only in cases of internal application of large quantities, say from 30 to 40 grains.

It is not advisable for sensitive persons to remain for a long time in a closed room where para-dichlorobenzene is freely exposed, as the odor may cause annoyance. On the other hand, para-dichlorobenzene can be used in closed or occasionally opened cupboards and even in sitting rooms without causing any inconvenience whatsoever.

PARA-DICHLOROBENZENE AS AN INSECTICIDE.

Experiments were conducted by the writer with para-dichlorobenzene to ascertain the practicability of its use and its insecticidal value against various insects. Para-dichlorobenzene as an insecticide is applicable to a large variety of insects, but under certain conditions depending on the variations in life history and environment, and therefore necessitating specific methods of application.

In a general way para-dichlorobenzene is effective only where its vapors can be closely confined, and when used in a higher temperature than 74° F.; furthermore, it is recommended only where poison bait and contact sprays are either impractical or undesirable. The vapor is diffused through the air very rapidly and must, therefore, be closely confined in order to maintain a sufficient proportion in the air to prove fatal to insect life.

The amount of material required, under ordinary conditions, to bring about the desired effect is about 12 ounces of para-dichlorobenzene to every 100 cubic feet of space. The writer, however, suggests the use of a larger amount, 1 pound to 100 cubic feet, which will take effect more quickly and diminish the chances of revival, although revival is aberrent. At temperatures between 75° and 85° F. an exposure of at least 36 hours is necessary for best results. Temperatures above 85° F. require only 24 hours exposure, due to the fact that heat facilitates the diffusion of the vapors.

Most warehouses and repositories contain several species of insects which possess very great tenacity of life, either in the adult or larval stages. In view of the fact that unless para-dichlorobenzene is used in enormous quantities or is permitted to remain in the respository over 48 hours, it does not injure plant life or render fruit, etc., inedible, we should, by preference, use as large a dose as possible for the complete eradication of the insects in the shortest possible time. As generally employed, the time would vary inversely to the amount of para-dichlorobenzene used. Since this substance is comparatively cheap and all unvolatilized material can be kept indefinitely, with very slight deterioration if the proper precautions are exercised, the additional amount of material required for a larger dose would be an insignificant item. Para-dichlorobenzene is insoluble in water and does not deliquesce when exposed to the air, but completely volatilizes, and should therefore be kept in an air-tight can or glass jar.

DIFFUSION OF THE VAPOR.

Para-dichlorobenzene is very volatile and the vapor is extremely heavy, being more than five times that of an equal volume of air and more than twice as heavy as carbon bisulphid vapor. Although it diffuses quite rapidly through the air, as evidenced by the perception of its odor, the vapors will, like carbon bisulphid, tend to work rapidly downward, outward, and eventually upward. From the foregoing fact it is ascertained that the greater density of vapor is at the lower levels. This property is obviously very beneficial when para-dichlorobenzene is used as a fumigant for bags of grain, stored products, carpets, and rugs, and in all cases where it is desirable to use a gas that will penetrate the lowest levels and force its way into cracks and crevices in floors, walls, and similar locations.

DIRECTIONS FOR USING.

Para-dichlorobenzene is applied in most instances in the same manner as camphor and naphthalene. It is not, however, necessary to sprinkle it around in corners or over rugs and other material, as is often the case with camphor and naphthalene, but merely to expose a sufficient quantity in one or two open or partially open receptacles, placed over, or higher, than the infested cases, goods, and material which require fumigation.

HOW PUT UP AND COST.

Para-dichlorobenzene at the present time is sold in 5, 10, 25, 50, and 100 pound and barrel lots, the prices for which are as follows:

23 cents per pound, in 5, 10, and 25 pound lots.
18 cents per pound, in 50-pound lots.
17 cents per pound, in 100-pound lots.
15 cents per pound, in barrel lots.

If any considerable quantity is to be used, it is much better to purchase of some wholesale druggist or direct from the manufacturers.

APPLICABILITY TO VARIOUS INSECTS.

Para-dichlorobenzene is applicable to many insect pests living under various conditions and environment, and therefore requires specific methods of application, and, unlike carbon bisulphid, it is at the present time used only indoors and in other places where its vapors can be closely confined. As there is a great variation in the tenacity of life among insects, the existing conditions should be carefully noted before para-dichlorobenzene is applied.

Beetles, such as the rice weevil (*Calandra oryza* L.), granary weevil (*Calandra granaria* L.), the confused flour beetle (*Tribolium confusum* Duv.), the cadelle (*Tenebroides mauritanicus* L.), the yellow

mealworm (*Tenebrio molitor* L.), and a few others less common are particularly hard to kill when in the adult stage. The larvæ of the mealworms, *Tenebrio molitor* L., *Tenebrio obscurus* L., and closely allied species, are likewise found by experiment to possess great tenacity of life. It is therefore recommended that a proportionately larger amount of para-dichlorobenzene be used when combating these species. Moths, flies, roaches, ants, and aphides are readily killed by para-dichlorobenzene when used in the ordinary strength recommended under the heading "Para-dichlorobenzene as an insecticide."

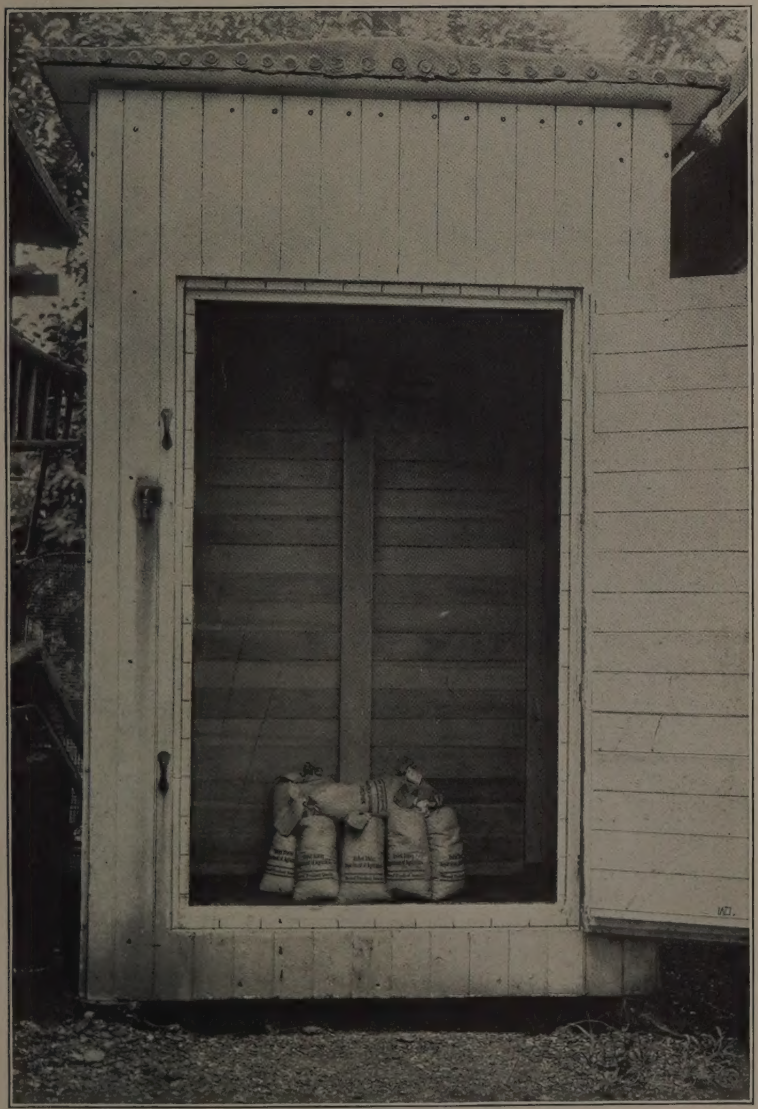
The action of para-dichlorobenzene on insects is primarily upon their nervous systems. This property is readily manifested when a moth is exposed to the vapors for a few seconds. It first displays great excitement and uneasiness, followed closely by spasmodic convulsions, and finally turns over on its back. While in this position violent nervous and muscular reflex action is noticed until life is extinct.

The moths on which this gas has been tested include the Angoumois grain moth (*Sitotroga cerealella* Oliv.), Mediterranean flour moth (*Ephestia kuehniella* Zell.), Indian meal moth (*Plodia interpunctella* Hbn.), meal snout moth (*Pyralis farinalis* L.), and the case-bearing clothes-moth (*Tinea pellionella* L.).

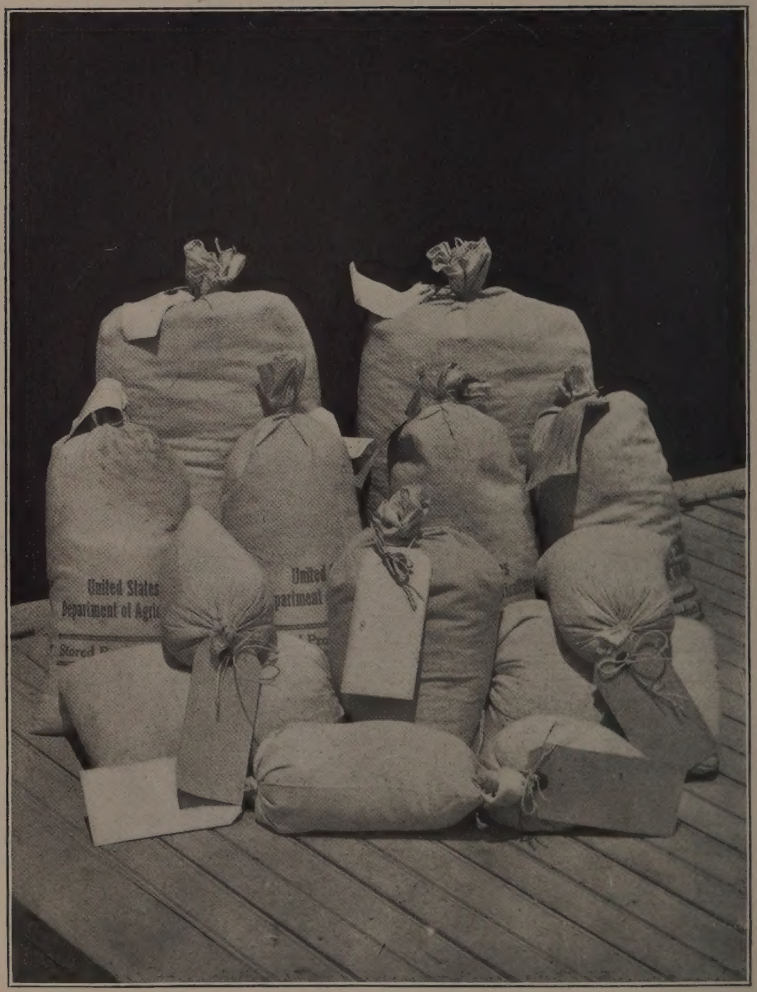
EXPERIMENTS WITH PARA-DICHLOROBENZENE AS A FUMIGANT.

During the spring of 1914, while stationed at Washington, D. C., the writer, working under the direction of Dr. F. H. Chittenden, performed a series of experiments with para-dichlorobenzene as a fumigant for stored-product insects. The chemical was first used on a small scale, and results were afterwards checked up in a specially constructed air-tight fumigating box having a capacity of 100 cubic feet (Pl. I.) The average temperature was computed from the records of a thermograph placed in the box, and the para-dichlorobenzene exposed in shallow piepans or the tops of 5-gallon lard cans, since these shallow receptacles present a much larger surface of the chemical for evaporation. These pans were placed about 4 feet above the material to be fumigated, which was contained in muslin bags of variable capacity (see Pl. II) and which had previously been ascertained to be free from live insects. Into this material, consisting of wheat, cornmeal, flour, rice, and other cereals, were then introduced living insects, the number and species of each being recorded on an attached tag.

The respective amounts of para-dichlorobenzene used in each experiment and the tabulated results follow.



FUMIGATING BOX USED IN EXPERIMENTS WITH PARA-DICHLOROBENZENE. (ORIGINAL.)



BAGS CONTAINING INFESTED GRAIN READY TO BE FUMIGATED WITH PARA-DICHLOROBENZENE.
(ORIGINAL.)

Experiments with para-dichlorobenzene as a fumigant.

Experiment No. and date.	Insects introduced.	Average temperature.	Length exposure.	Date examined.	Para-dichlorobenzene used.	Per cent killed.	Remarks.
		° *F.*	*Hours.*				
No. 1, Mar. 25, 1914.	Tribolium confusum Duv.; T. ferrugineum Fab.; Calandra oryza L.; C. granaria L.; Silvanus surinamensis L.; Rhizopertha dominica Fab.; Laemophloeus minutus Oliv.; Tenebrio molitor L.; Sitotroga cerealella Oliv.; Plodia interpunctella Hbn.; Ephestia kuehniella Zell.	52	72	Apr. 1	1 ounce.	None.	All revived. Preliminary ttest. Temperature too low. Vapors diffused very slowly. Eggs, larvæ, pupæ, and adults used in the case of Ephestia kuehniella and Plodia interpunctella. Capacity of fumigating box used, 7 cubic feet.
No. 2, Apr. 7, 1914.	Same as in experiment No. 1.	59	96	Apr. 13	8 ounces.	None.	All revived. Preliminary test. Temperature too low. Fumigating box used, 7 cubic feet.
No. 3, Apr. 18, 1914.	Same as in experiment No. 1.	65	96	Apr. 25	8 ounces.	20	Unsatisfactory. Preliminary test. Fumigating box used, 7 cubic feet.
No. 4, Apr. 28, 1914.	Tribolium confusum Duv.; T. ferrugineum Fab.; Calandra oryza L.; C. granaria L.; Silvanus surinamensis L.; Rhizopertha dominica Fab.; Sitotroga cerealella Oliv.; Plodia interpunctella Hbn.; Ephestia kuehniella Zell.; (Bruchus) Pachymerus 4-maculatus Fab.	81	24	May 5	2 pounds	100	100 cubic feet fumigating box used for this experiment.
No. 5, Apr. 29, 1914.	Roaches	80	24	May 2	2 ounces.	100	5 cubic feet fumigating jar used.
No. 6, May 1, 1914.	Mites on corn	78	28	May 5	2 ounces.	100	5 cubic feet fumigating jar used.
No. 7, May 4, 1914.	Slugs, snails, sowbugs, millipedes, ants.	82	36	May 9	2 pounds	100	100 cubic feet fumigating box used.
No. 8, May 11, 1914.	Tribolium confusum Duv.; Calandra oryza L.; Silvanus surinamensis L.; Sitotroga cerealella Oliv.; Plodia interpunctella Hbn.; Ephestia kuehniella Zell.; Laemophloeus minutus Oliv.; Tenebrio molitor L.	86	24	May 16	2 pounds	100	100 cubic feet fumigating box used in this experiment. Four bricks were heated to a high temperature and placed in box in order to obtain higher temperature.
No. 9, May 14, 1914.	Same as in experiment No. 8.	73	24	May 20	2 pounds	70	Unsatisfactory. Temperature too low.
No. 10, May 15, 1914.	Flies	81	20	May 16	8 ounces.	100	100 cubic feet space.
No. 11, May 18, 1914.	Aphides	80	20	May 19	8 ounces.	100	100 cubic feet space.

No. 12. May 19, 1914, 4 ounces of finely ground para-dichlorobenzene were sprinkled over pieces of woolen cloth and placed in a 100-cubic-foot fumigating box for a period of 24 hours, at an average temperature of 76° F. Upon examination it was discovered that the fine crystals adhered to the lint of the wool but were readily brushed off with a whisk broom. After two hours' exposure in the open air the odor of para-dichlorobenzene was barely perceptible.

No. 13. May 20, 1914, a test on the germination of seed was made. One pint of Argentine corn, about half of which had previously sprouted, was put in a 7-inch flower pot containing 4 inches of moist fertile soil. The pot was then introduced into a 100-cubic-foot fumigating box and exposed to the vapors of para-

dichlorobenzene for 24 hours at an average temperature of 79° F. Two days later the seed was examined and showed no material injury from the experiment, sprouting about as usual.

NOTE.—Preliminary experiments with para-dichlorobenzene have been conducted along the following lines: 1. Para-dichlorobenzene introduced into insect collection boxes for the eradication of museum pests. 2. Para-dichlorobenzene in combination with formaldehyde and potassium permanganate as an insecticide and germicide. 3. Para-dichlorobenzene made into a paste by adding paraffin and resin in the presence of heat, as a substitute for grafting wax. The above paste to be applied in the burrows of borers in shade trees. 4. Further experiments on the effect of para-dichlorobenzene, if any, on tender plants. 5. The effects, if any, of para-dichlorobenzene on animals, when taken internally in small doses. In these experiments green food, such as kale, cabbage, and clover, were put in a jar heavily charged with para-dichlorobenzene vapors and fed twice daily to herbivorous animals, such as rabbits and guinea-pigs. In these experiments the writer has not as yet reached any definite conclusions, and therefore reserves their publication until further experiments along these lines are completed.

CONCLUSION.

From the foregoing observations and experiments the writer concludes that para-dichlorobenzene, used as directed in the preceding pages, acts as an excellent fumigant against the following insects:

(1) Stored-product insects.
(2) Case-bearing clothes moths.
(3) Roaches and ants.
(4) Museum pests.
(5) Miscellaneous house insects, including flies, carpet beetles or buffalo moths, book lice, silverfish, mosquitoes, centipedes, and miscellaneous larder insects.

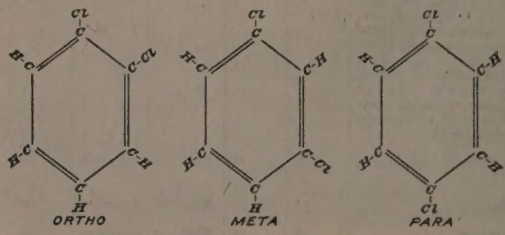
It is also an effective substitute for potassium cyanid in collecting bottles.

CHEMICAL AND PHYSICAL PROPERTIES OF PARA-DICHLOROBENZENE.

At the request of Dr. Chittenden the following data were kindly furnished by the Insecticide and Fungicide Laboratory, Miscellaneous Division, Bureau of Chemistry:

We have made an examination of the sample of dichlorobenzene submitted by you for examination on December 22, 1913, and find that this product is practically pure para-dichlorobenzene ($C_6H_4Cl_2$). We have looked up some references in the literature in regard to this substance and give you the following information based thereon:

Dichlorobenzene is a product derived from benzene by the replacement of two of the hydrogen atoms by chlorine. There are three dichlorobenzenes, designated ortho, meta, and para, the structural formulas of which are:



All three have the empirical formula $C_6H_4Cl_2$. Ortho and meta dichlorobenzenes are liquids, the former boiling at 179° C. and the latter at 172° C.

Beilstein, in his Handbuch der organischen Chemie, III Auflage, 1896, Band II, page 44, gives three methods for the preparation of para-dichlorobenzene (in the German, p-dichlorbenzol):

(1) By the action of chlorine on benzene (C_6H_6) in the presence of iodine. A little ortho-dichlorobenzene is also formed in this reaction.

(2) By the action of phosphorus pentachlorid on para-chlorophenol.

(3) By the action of phosphorus pentachlorid on para-phenolsulphonic acid.

He gives the melting point of this compound as 53° C. (127.4° F.) and its boiling point as 172° C. (341.6° F.), but quotes Mills (Phil. Mag. (5) 14, 27) as giving 52.72° C. for the melting point.

Para-dichlorobenzene crystallizes from alcohol in monoclinic leaves, it sublimes at ordinary temperatures, is soluble in hot alcohol in all proportions, and is easily soluble in ether, benzene, carbon bisulphid, etc.

In regard to physiological properties, Francis and Fortescue-Brickdale [1] state:

The benzene halogen derivatives have a slight odor, are insoluble in water, volatilize without decomposition, and are very stable. * * * Corresponding to their stability it is found that the halogen is not split off in the organism, and that they do not show hypnotic properties. With the entrance of chlorine the antiseptic properties increase * * * Chlorbenzene acts on the spinal cord to a greater extent than benzene.

The following figures in regard to para-dichlorobenzene are from calculations made by R. C. Roark:

Molecular weight	146.952	
Density of the vapor	4.592	if oxygen equals 1.
	72.892	if hydrogen equals 1.
	5.1025	if air equals 1, assuming the molecular weight of air to be 28.8.

In other words, assuming no dissociation or association, a given volume of para-dichlorobenzene in the form of a vapor would be 5.1025 times as heavy as an equal volume of air at the same temperature and at the same barometric pressure.

The vapor of para-dichlorobenzene will flash at about 70° C. (158° F.), but even when held in a very hot flame and ignited the substance will not continue to burn after the flame is removed. Thus the substance is not combustible, but is decomposed by heat into substances which partially burn with copious deposition of soot when directly in a flame.

As the vapor pressure of para-dichlorobenzene has never been determined, it is impossible to state how much of its vapor air at any temperature short of 172° C. (341.6° F., its boiling point) would take up. At 172° C. (341.6° F.), barometer 760 mm., 1 liter of para-dichlorobenzene gas would weigh 4.0257 grams, or 1 cubic foot would weigh 4.0208 avoirdupois ounces.

[1] Francis, Francis, and Fortescue-Brickdale, J. M. The Chemical Basis of Pharmacology, p. 99, London, 1908.

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